SOME ASPECTS OF CHLORINATION

By Joseph Race

Although the treatment of water by chlorine or hypochlorite has been very extensively practised for several years, it is a regrettable fact that comparatively few investigations have been made into this process with a view to elucidating the basic principles and the modifications required to meet various conditions.

When chlorination was first introduced for the sterilization of water and sewage, all that was required was the addition of the hypochlorite; after this the process was supposed to take care of itself. Now we realize that, to obtain the best results, the process requires careful supervision and close attention to certain points. It is the purpose of the author to draw attention to some of these details in this paper.

1. MECHANICAL ADMIXTURE

Due attention has not always been given to this phase of the chlorination problem because of the prevalent opinion that the all important point was contact period. The author has previously recorded[1] experiments made for the purpose of comparing the importance of these two factors. In 1914 a sedimentation basin was placed in operation at the mouth of the Ottawa intake pipe, and during July the hypochlorite solution was added at the entrance to this basin. The method of addition was by means of a perforated pipe which stretched across the entrance to the basin, and the bleach solution and water were there mixed as thoroughly as was possible without having recourse to mechanical methods. The basin was baffled and had a normal capacity equal to approximately two hours consumption (1.7 millions imperial gallons). The results obtained were as follows:

[1] *J. Soc. Chem. Ind.*, 1912, 31, 611–616, and 1915, 34, 931–934.

Available chlorine = 1.88 parts per million. Bacteria per cubic centimeter

	AGAR THREE DAYS AT 20° C.	AGAR ONE DAY AT 37° C.	B. COLI INDEX PER CC.
Raw water	410.0	104.0	0.280
Treated water	49.0	26.0	0.036
Percentage purification	88.2	75.0	87.500

During August the connection at the entrance to the basin was closed and the bleach liquor added directly to the suctions of the low lift pumps, which take water from the sedimentation basin and place it in the intake pipe under a small positive pressure until it reaches the high lift pumps. During both months the samples of treated water were taken from the well which receives the mixed discharges of the low lift pumps. The results for August were:

Available chlorine = 1.55 parts per million. Bacteria per cubic centimeter

	AGAR THREE DAYS AT 20° C.	AGAR ONE DAY AT 37° C.	B. COLI INDEX PER CC.
Raw water	448	100	0.600
Treated water	26	12	0.005
Percentage purification	91.9	88.0	99.200

These results, which are the averages of daily analyses, show that the efficient mechanical admixture produced much superior results with a smaller consumption of chlorine.

COLOR

The effect of color, as is well known, is to reduce the efficiency of chlorination and to necessitate the use of a much larger dose. This is well exemplified in the following table which gives the results of chlorination experiments on B. coli seeded into water. Water "B" was the raw Ottawa River water containing 40 parts per million of color, and Water "A," with a color of 3 parts per million, was produced from "B" by precipitating with sulphate of alumina and subsequently filtering. The B. coli count was made by platting out 10 cc. of water in neutral red bile salt agar and counting the typical red colonies. Counts were made after 24, 48 and 72 hours, but in this table only the 24 hour count is recorded. The counts at later

periods were made to determine whether the organisms were actually killed or the reproductive capacity merely delayed, as was observed on a former occasion.[2] In none of the experiments was any evidence obtained of any revival of the organisms.

TABLE 1

Colonies per 10 cc. of water. Temperature = 63° F.

CONTACT PERIOD	WATER "A." COLOR 3	WATER "B." COLOR 40		
	Available chlorine p. p. m.	Available chlorine p. p. m.		
	0.2	0.2	0.4	0.5
Nil	194	194	194	194
5 minutes	121	165	129	66
1 hour	7	95	20	1
5 hours	0	4	0	0
24 hours	0	1	1	0
48 hours	0	0	0	0

To obtain the same result with about one hours' contact at 63° F., it is necessary to use about two and one-half times as much chlorine with a water of color 40 as with one practically free from color. Somewhat similar results have been obtained at Montreal by Harrington.[3] For the greater part of the year St. Lawrence water free from color is obtained at the inlet at the Montreal intake pipe, and only requires approximately 0.3 parts per million of available chlorine for satisfactory treatment. During the spring floods the currents are altered and the Ottawa River water is obtained; this requires as much as 1.5 parts per million of chlorine, but a portion of this high dose is necessitated by the increase of turbidity. During the flood period the color is somewhat reduced but its effect in the chlorination efficiency is more than counterbalanced by the increase in turbidity.

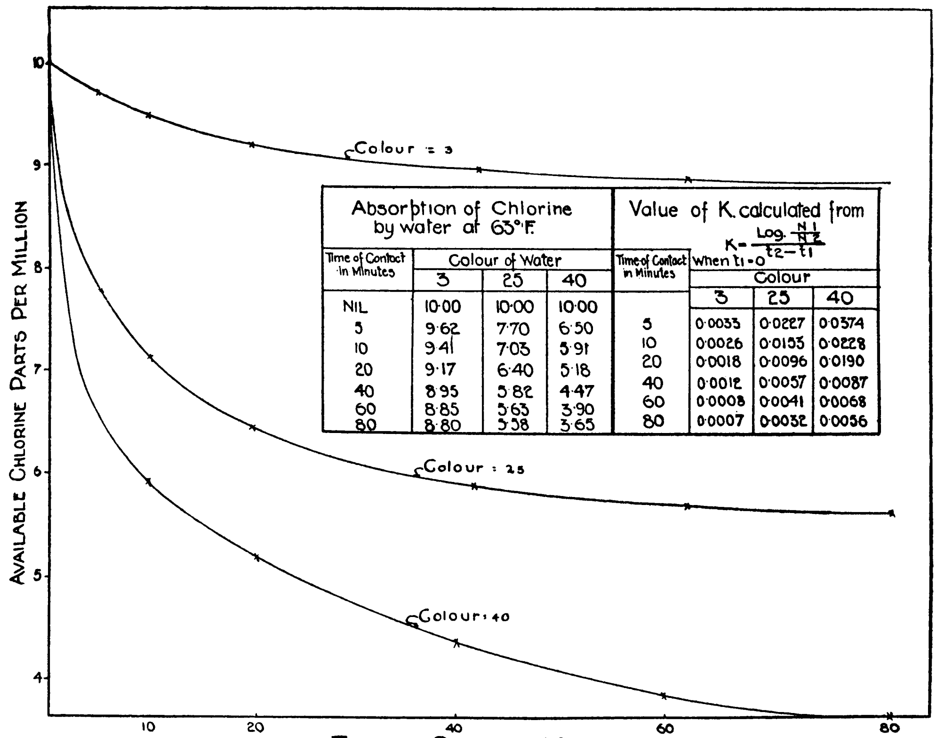
The effect of color upon the absorption of chlorine, in the form of hypochlorite, by water, is well shown in diagram 1. The absorption takes the form of a monomolecular reaction, the mathematical expression of this law being $\frac{dN}{dt} = KN$ where N is the concentration of the available chlorine in parts per million. Integrating between

[2] *J. Soc. Chem. Ind.*, 1912, 31, 611–616.

[3] Vide this Jour., Vol. I, No. 3, p. 438.

t_1 and t_2 we get the formula $K = \frac{\log \frac{N_1}{N_2}}{t_2 - t_1}$. If the compound absorbing the chlorine were simple in character, the value of K found would be constant in each experiment. Instead of that we find a constantly diminishing quantity, which is explained by the fact that the compound acted upon is not simple but a mixture of complex molecules having different affinities for oxygen.

DIAGRAM No. 1



Absorption of Chlorine by water at 63°F.				Value of K calculated from $K = \frac{\log \frac{N_1}{N_2}}{t_2 - t_1}$ when $t_1 = 0$			
Time of Contact in Minutes	Colour of Water 3	25	40	Time of Contact in Minutes	Colour 3	25	40
NIL	10·00	10·00	10·00				
5	9·62	7·70	6·50	5	0·0033	0·0227	0·0374
10	9·41	7·03	5·91	10	0·0026	0·0153	0·0228
20	9·17	6·40	5·18	20	0·0018	0·0096	0·0190
40	8·95	5·82	4·47	40	0·0012	0·0057	0·0087
60	8·85	5·63	3·90	60	0·0008	0·0041	0·0068
80	8·80	5·58	3·65	80	0·0007	0·0032	0·0056

EFFECT OF COLOUR ON ABSORPTION OF CHLORINE BY WATER

TEMPERATURE

The effect of temperature on a culture of B. coli in unsterilized water, color 40, is well illustrated in the two following tables.

TABLE 2

Effect of Temperature

Colonies per 10 cc. of water. Available chlorine 0.4 parts per million

CONTACT PERIOD	TEMPERATURE, DEGREES, FAHRENHEIT,		
	36	70	98
Nil	424	424	424
5 minutes	320	280	240
1.5 hours	148	76	12
4.5 hours	38	14	3
24 hours	2	0	0
48 hours	2	0	0

TABLE 3

Colonies per 10 cc. of water. Available chlorine 0.2 parts per million

CONTACT PERIOD	TEMPERATURE, DEGREES, FAHRENHEIT,		
	36	70	98
Nil	240	240	240
5 minutes	240	250	235
1 hour	245	235	195
4 hours	215	190	170
24 hours	143	130	115
48 hours	130	59	19
72 hours		28	
96 hours		16	
120 hours		6	

In the 70° F. experiment the sample, after 3, 4 and 5 days contact, was innoculated into lactose bile and lactose broth with the following results:

CONTACT PERIOD	LACTOSE		B. COLI PER 10 CC. MOST PROBABLE NUMBER		COLONIES PER 10 CC. ON REBIPEL-AGAR
	Bile	Broth	Lactose bile	Lactose broth	
72 hours	2/5	5/5	5	20	28
96 hours	0/5	4/5	1	16	16
120 hours	0/5	2/5	1	5	6

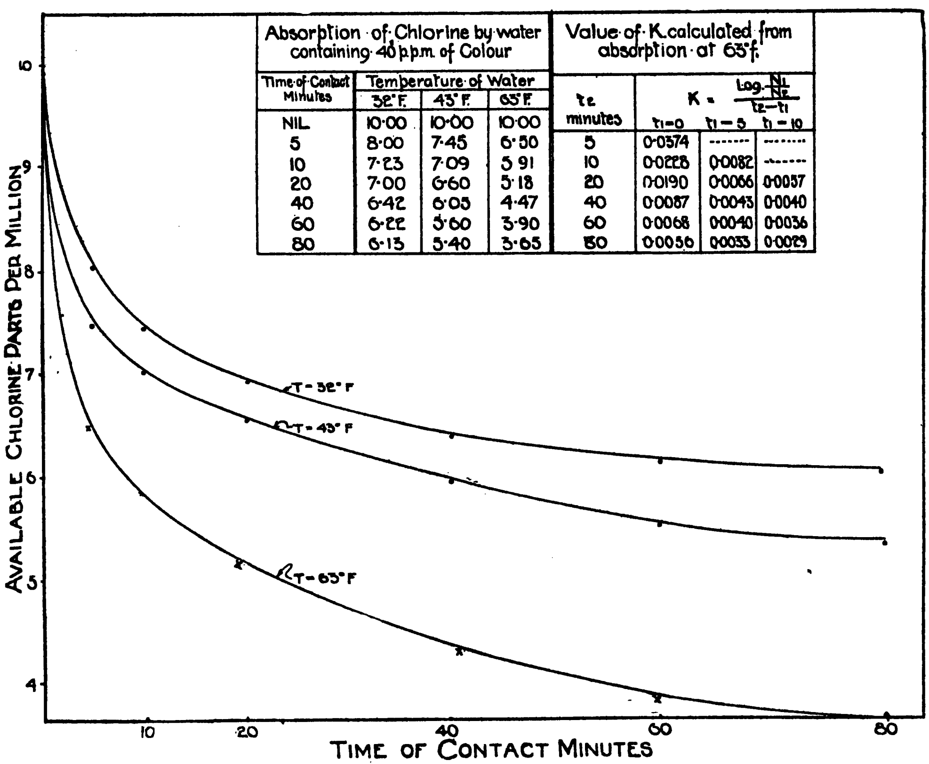
When these results are calculated to the most probable numbers by McCrady's method[4] some interesting comparisons are obtained. The lactose broth and rebipelagar plates are in close agreement but

[4] *Jour. Inf. Dis.*, 1915, 17, 183–212.

yield results very much higher than the lactose bile. If lactose bile only takes account of virile organisms it must be assumed that the majority of the B. coli remaining after 72 hours contact are attenuated. This dictum would appear to be somewhat arbitrary and empirical.

The effect of temperature upon the absorption of the available chlorine is shown in diagram 2.

DIAGRAM No. 2



Absorption of Chlorine by water containing 40 p.p.m. of Colour			
Time of Contact Minutes	Temperature of Water		
	32° F.	43° F.	65° F.
NIL	10·00	10·00	10·00
5	8·00	7·45	6·50
10	7·23	7·09	5·91
20	7·00	6·60	5·18
40	6·42	6·05	4·47
60	6·22	5·60	3·90
80	6·13	5·40	3·65

Value of K calculated from absorption at 65° f.			
t_2 minutes	$K = \frac{\log \frac{N_1}{N_2}}{t_2 - t_1}$		
	$t_1 = 0$	$t_1 = 5$	$t_1 = 10$
5	0·0374	-------	-------
10	0·0228	0·0082	-------
20	0·0190	0·0066	0·0057
40	0·0087	0·0043	0·0040
60	0·0068	0·0040	0·0036
80	0·0056	0·0033	0·0029

AFTERGROWTHS

In connection with chlorination, many well authenticated reports have been made that, after the preliminary germicidal action has subsided, a second phase occurs in which there is an accelerated growth of organisms. This is usually known as aftergrowth. When there

is only a short contact period between chlorination and consumption the reaction does not proceed beyond the first phase, but when the treated water is stored in service reservoirs the second phase may ensue, and is usually ascribed to a change in pabulum effected by the action of the chlorine or oxygen on the organic matter. Regarding the nature of this aftergrowth there has been considerable difference of opinion; some hold that it is the result of the multiplication of a resistant minority of practically all the species present in the untreated water; others that it is partially due to the bacteria being merely "slugged" or "doped," i.e., in a state of suspended animation, and afterwards resuming their anabolic functions; whilst others believe that, with the proper dose of chlorine, only spore forming organisms escape destruction and that the aftergrowth is the result of these cells again becoming vegetative. The aftergrowths obtained under the usual working conditions vary according to the dosage of chlorine employed, and none of the above hypotheses alone provides an adequate explanation. When the dosage is small a small number of active organisms, in addition to spore bearers, will escape destruction, and others, as was shown by the author in a previous paper,[5] will suffer a reduction of reproductive capacity. The flora of the aftergrowth in this case will only differ from the original flora by the elimination of species that are very susceptible to chlorine. As the dose is increased these two factors become relatively less important, until a stage is reached when only the most resistant cells, the spores, are left. The resultant aftergrowth must necessarily be entirely composed of spore forming organisms. Chlorination operators do not usually use a dose that would eliminate all but spore bearers, and it therefore becomes essential that we should know whether the aftergrowth has any sanitary significance. Concerning the secondary development of B. coli, the usual index of pollution, there is but very meager information. H. E. Jordan[6] reported that of 201 samples, 21 gave a positive B. coli reaction immediately after treatment, 39 after 24 hours standing and 42 after 48 hours. These increases were confined to the warm months, the cold months actually showing a decrease. The following figures taken from the author's routine tests for 1913 and 1914 show a similar tendency but an analysis of the results by months did not show that this was confined to the summer months.

[5] *Jour. Soc. Chem. Ind.*, 1912, 31, pp. 611–616.

[6] *Eng. Rec.*, 1915, May 17.

The sequence of the results from left to right in the following table is in the same order as the contact period, and each percentage represents the average of approximately 290 samples.

Percentage of samples showing B. Coli in 10 c.c.m.

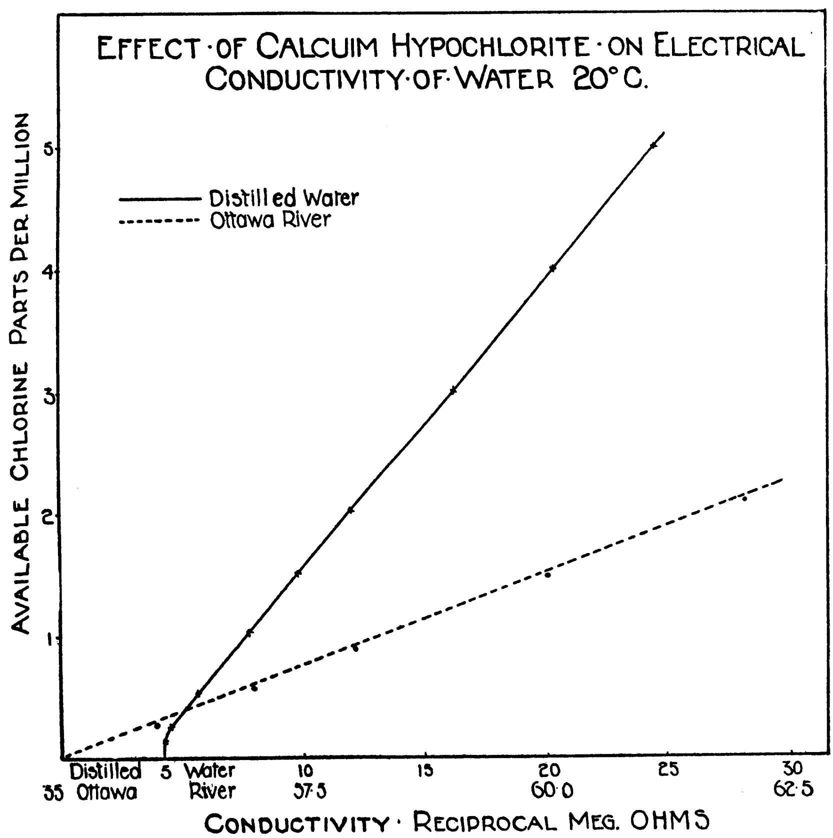
	1	2	3	4	5
1913	15.2	14.4	16.3	16.8	26.8
1914	7.0	5.7	6.0		11.6

At station 2 the germicidal action was evidently still proceeding but at station 5, representing an outlying section of the city, the increase is marked.

During 1915 and 1916 the author attempted to duplicate these results under laboratory conditions and entirely failed. Usually these experiments, which were made with the same materials as were in use at the city plant, but in glass containers, were only carried to 48 hours contact as this would be the extreme limit found in practice; one, however, was prolongued to 5 days. Many experiments of this nature were made with varying conditions, but as the results are all similar there is nothing to be gained by adding to those given in tables 1, 2 and 3. In every case there is a persistent diminution in the number of B. coli organisms found with increase of contact period. Determination of the bacterial count on nutrient agar showed in several cases that the aftergrowth had commenced, and in some instances there was evidence that the second cycle was partially complete, i.e., the number had reached a maximum and then commenced to decline. The time required for the completion of the two cycles, comprising the first reduction caused by the chlorine, the increase or aftergrowth and the final reduction due to lack of suitable food material, is dependent upon various factors of which the dosage and temperature are the most important. With a small dosage the germicidal period is short and the second phase quickly reached; with large doses the second phase is not reached within 48 hours. Low temperatures reduce the velocity of the germicidal action but extend the period over which it is effective. The higher the temperature the quicker is the action and the development of the aftergrowth. These statements refer only to the total bacteria as found by development on nutrient agar. The B. coli did not act in this way and persistently diminished in every case. If B. Typhosus acts

in a similar manner to B. coli, the laboratory experiments show that aftergrowths are of no sanitary significance, and can safely be ignored, but as the results obtained in actual practice are apparently contradictory the matter should be regarded as "sub judice" until more definite evidence is available. Perhaps the remarkable photochemical properties of chlorine are concerned in this matter.

DIAGRAM No. 3



CORROSION

Numerous complaints regarding corrosion of piping systems in Ottawa led to the routine determination of free carbonic acid in the raw and treated waters. During a period of excessive turbidity and

pollution a very heavy dose of chlorine was used and an increase in the free carbonic acid resulted. During the past 18 months the average results show a decrease so that there could scarcely be an increased corrosive action due to carbonic acid.

If the treatment is considered according to the electrolytic theory, a slight increase in corrosion might be expected due to an increased electrical conductivity. The conductivities of various chlorinated mixtures were therefore determined with the results as shown in diagram 3.

With the usual dosages of chlorine it is inconceivable that the increased electrical conductivity has any practical significance at ordinary temperatures. At temperatures approaching the boiling point of water the percentage increase in conductivity would be somewhat greater, and may possibly assume practical importance.

SURVIVING TYPES OF B. COLI

Several experiments were made with a view to ascertaining whether the B. coli found after chlorination were more resistant to chlorine than the original culture. The colonies surviving after treatment with comparatively large doses were fished into lactose broth and this culture used for a second chlorination. The surviving organisms were again fished and the process repeated several times. The velocity of the chlorination reaction varied somewhat, but not always in the same direction, and the variations were not greater than were found in duplicate experiments with the original culture. No evidence was obtained that the surviving organisms were in any way more resistant to chlorine than the original culture. It should be remembered, however, that the surviving types were cultivated twice on media free from chlorine before being again subjected to chlorination. A number of the colonies surviving several chlorinations were cultivated in lactose broth, and the acidity determined quantitatively. All the cultures produced less acid than the original culture, and the average was materially less than the original cultivated under the same conditions. This points to a diminution in the biochemical activity.

A point of perhaps more scientific interest than practical utility is the relative proportion of the various types of B. coli found before and after treatment with chlorine. The author in 1914 commenced the analysis of the various types using the division of the American

Public Health Association by dulcite and saccharose as a basis. The averages of a large number of samples were as shown in table 4.

TABLE 4

	B. COLI COMMUNIS		B. COLI COMMUNIOR		B. LACTIS AEROGENES		B. ACIDI LACTICI	
	Raw	Chlorinated	Raw	Chlorinated	Raw	Chlorinated	Raw	Chlorinated
Ottawa, 1914	5	4	40	48	44	36	11	12
Ottawa, 1915	8	8	50	46	34	31	8	15
Baltimore, 1913*	11	14	33	25	35	31	21	30

* Thomas and Sandman, *J. Ind. and Eng. Chem.*, 1914, 6, p. 638.

Although there is a slight difference in the relative proportions of the types found at Ottawa and Baltimore, both sets of results show definitely that there is no difference in the resistance of the various types to chlorine.